

PCT

WORLD INTELLECTUAL PROPERTY ORGANIZATION  
International Bureau



INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification <sup>6</sup> : <b>B32B 27/18, 27/36, C08K 5/00, 5/315, 5/35, C08L 67/00, 33/00, 69/00</b>	A1	(11) International Publication Number: <b>WO 98/19862</b> (43) International Publication Date: <b>14 May 1998 (14.05.98)</b>
---	----	---

(21) International Application Number: <b>PCT/US97/19895</b> (22) International Filing Date: <b>3 November 1997 (03.11.97)</b>  (30) Priority Data: 08/743,351 4 November 1996 (04.11.96) US  (71) Applicant: EASTMAN CHEMICAL COMPANY [US/US]; 100 North Eastman Road, Kingsport, TN 37660 (US).  (72) Inventors: FAGERBURG, David, Richard; 3812 Cimmaron Drive, Kingsport, TN 37664 (US). VICARS, Jack, Donald; 2744 Circle View Drive, Kingsport, TN 37664 (US).  (74) Agent: TUBACH, Cheryl, J.; P.O. Box 511, Kingsport, TN 37662-5075 (US).	(81) Designated States: CN, JP, European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).  Published <i>With international search report. Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i>
--	--

(54) Title: UV STABILIZED MULTI-LAYER STRUCTURES WITH DETECTABLE UV PROTECTIVE LAYERS AND A METHOD OF DETECTION

(57) Abstract

A UV stabilized multi-layer structure which has an easily visible UV protective layer comprises a UV protective layer and an underlying polymeric layer. The polymeric layer is either a polyester or a polycarbonate. The UV protective layer, which is exposed to UV radiation and protects the polymeric layer, comprises a UV absorbing compound, an optical brightener present in an amount sufficient to cause visual illumination of the UV protective layer upon exposure to a light source and a polymeric base material of either a polyester, polycarbonate or acrylic. Upon exposure to a UV light or white light source the UV protective layer is visibly illuminated. A method of detecting the UV protective layer in the UV stabilized multi-layer structure is also provided.

**FOR THE PURPOSES OF INFORMATION ONLY**

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AL	Albania	ES	Spain	LS	Lesotho	SI	Slovenia
AM	Armenia	FI	Finland	LT	Lithuania	SK	Slovakia
AT	Austria	FR	France	LU	Luxembourg	SN	Senegal
AU	Australia	GA	Gabon	LV	Latvia	SZ	Swaziland
AZ	Azerbaijan	GB	United Kingdom	MC	Monaco	TD	Chad
BA	Bosnia and Herzegovina	GE	Georgia	MD	Republic of Moldova	TG	Togo
BB	Barbados	GH	Ghana	MG	Madagascar	TJ	Tajikistan
BE	Belgium	GN	Guinea	MK	The former Yugoslav Republic of Macedonia	TM	Turkmenistan
BF	Burkina Faso	GR	Greece	ML	Mali	TR	Turkey
BG	Bulgaria	HU	Hungary	MN	Mongolia	TT	Trinidad and Tobago
BJ	Benin	IE	Ireland	MR	Mauritania	UA	Ukraine
BR	Brazil	IL	Israel	MW	Malawi	UG	Uganda
BY	Belarus	IS	Iceland	MX	Mexico	US	United States of America
CA	Canada	IT	Italy	NE	Niger	UZ	Uzbekistan
CF	Central African Republic	JP	Japan	NL	Netherlands	VN	Viet Nam
CG	Congo	KE	Kenya	NO	Norway	YU	Yugoslavia
CH	Switzerland	KG	Kyrgyzstan	NZ	New Zealand	ZW	Zimbabwe
CI	Côte d'Ivoire	KP	Democratic People's Republic of Korea	PL	Poland		
CM	Cameroon	KR	Republic of Korea	PT	Portugal		
CN	China	KZ	Kazakhstan	RO	Romania		
CU	Cuba	LC	Saint Lucia	RU	Russian Federation		
CZ	Czech Republic	LI	Liechtenstein	SD	Sudan		
DE	Germany	LK	Sri Lanka	SE	Sweden		
DK	Denmark	LR	Liberia	SG	Singapore		
EE	Estonia						

- 1 -

UV STABILIZED MULTI-LAYER STRUCTURES WITH  
DETECTABLE UV PROTECTIVE LAYERS  
AND A METHOD OF DETECTION

5

TECHNICAL FIELD

This invention relates to polyester or polycarbonate multi-layer structures that are exposed to ultraviolet radiation. More particularly, this invention relates to a method for detecting an 10 ultraviolet protective layer in the structure.

BACKGROUND OF THE INVENTION

Polyesters and polycarbonates are not very stable to the effects of ultraviolet (UV) radiation. Exposure 15 to UV radiation over extended periods of time causes hazing, property loss and yellowing. This lack of property stability upon exposure to UV radiation has long limited the uses of these materials in outdoor environments.

The addition of UV absorbing compounds, sometimes called UV stabilizers, are used to retard the loss of properties and particularly the development of yellow coloration in polyester or polycarbonate structures exposed to UV radiation. The UV absorbing compounds 25 must have an extinction coefficient significantly higher than that of the polymers to be stabilized such that almost all of the incident UV radiation is absorbed by the compounds rather than the polymers. The energy absorbed by the UV absorbing compounds is harmlessly transferred to the polymers as heat rather than transferred electronically to the polymer chains. The fragmentation of the chains is thereby suppressed and the properties of the polymers are retained for a longer 30 time of exposure. Thus, polyesters and polycarbonates

- 2 -

that contain the UV absorbing compounds may be used in applications that have exposure to UV radiation.

The polyesters and polycarbonates structures containing UV absorbing compounds are typically used in sheet form. Sheeting made from clear, colored or pigmented polymers is advantageously employed in a great number of outdoor applications when the sheeting has sufficient color stability, mechanical property retention and thermoformability. The back side of the sheeting may also be printed on or have a decorated sheet adhered thereto. Representative applications include signs and marquees; vehicle luggage carriers; solar roof panels; skylights; highway sound barriers; greenhouse panels; aquarium walls; parts for motor and recreational vehicles such as windows, roofs, body panels, bug and air deflection screens and vents; transparent or translucent awnings; formed letters for application to buildings; airport runway marker signs; multiwall sheeting for use in signs; and facia for soft drink and juice dispensing machines.

For economic reasons, the UV stabilized polyester or polycarbonate structures are typically multi-layer having a UV protective layer, which is exposed to UV radiation, and an underlying polymeric layer, which is protected from the effects of UV radiation by the UV protective layer. The UV protective layer contains the UV absorbing compound and a polymeric base material of a polyester, polycarbonate or acrylic depending on the end use. The polymeric layer is typically a polyester or polycarbonate. The UV protective layer is typically either laminated or coextruded onto the polymeric layer. The UV protective layer performs its protective function as a relatively thin film as compared to the polymeric layer, thereby providing cost reduction by reducing the amount of UV absorbing compound needed.

- 3 -

The UV stabilized multi-layer structures may be sheets, films, profiles, or hollow profiles depending on the final use of the UV stabilized structures. The hollow profiles are typically made by connecting two or 5 more sheets with ribbings running the length of the sheeting. The ribbings are spaced so as to provide structural stiffness to the final structures that would otherwise not be present. The ribbings make continuous channels down the length of the structure.

UV absorbing compounds are typically either fluorescing or non-fluorescing. Benzotriazoles, triazines and diphenylcyanoacrylates are useful as non-fluorescing UV stabilizers for polyesters and polycarbonates. Benzoxazinones are particularly useful 10 as fluorescing compounds for various polymers, including polyesters, polyamides, polycarbonates, polyolefins and polysulfones. Additional UV absorbing fluorescing 15 compounds are those that result from the substitution of various functional groups onto the aromatic ring(s) of the benzoxazinone system. The functional groups affect 20 a shift in the wavelength of absorption of the compound or render it reactive with or copolymerizable into a polyester matrix. For example, an oligomer containing benzoxazinone units is blended with a polyester to give 25 a copolymerized UV absorbing unit with permanence.

In the UV stabilized multi-layer structures, the UV protective layers are often extremely difficult to visualize accurately causing human error in labeling the 30 sides of the structures to be exposed to UV radiation sources. This is especially so in a production environment when speed is required. The non-fluorescing UV absorbing compounds, even under illumination with UV light, do not fluoresce well if at all. The fluorescing UV absorbing compounds, while visible under illumination 35 with a long wave UV light, are still difficult to

- 4 -

detect. As the UV protective layer becomes thinner, it becomes more difficult to determine its presence and accurately measure its thickness. The boundary between the UV protective layer and the polymeric layer becomes  
5 more difficult to see as the total visual signal to the eye becomes less as the thickness diminishes. Additionally, the exciting wavelength of the UV absorbing compound is relatively short; thus, the UV protective layers do not show up when the multi-layer  
10 structures are illuminated with UV light from the sides opposite to the UV protective layers. Confusion of production personnel may occur since no fluorescing layers are seen, only an overall purple glow of the polymeric materials.

15 The difficulty of visualizing the UV protective layers creates problems not only during production, but also during installation of precut panels of the UV stabilized multi-layer structures. On such panels the sides to be exposed toward the sun are typically labeled  
20 on the masking film of the panels. During the process of constructing a greenhouse, for example, the protective masking of the panels may be removed and the panels not immediately installed. When the panels are later installed, the worker may no longer be certain  
25 which side should face the sun. The potential for costly error is obvious.

Thus, there exists a need in the art for a simple, inexpensive method to detect the presence of the UV protective layers to enable accurate labeling and  
30 installation of UV stabilized multi-layer structures. Accordingly, it is to the provision of such method that the present invention is primarily directed.

- 5 -

SUMMARY OF THE INVENTION

A UV stabilized multi-layer structure which has an easily visible UV protective layer comprises a UV protective layer and an underlying polymeric layer. The 5 polymeric layer is either a polyester or a polycarbonate. The UV protective layer, which is exposed to UV radiation and protects the polymeric layer, comprises a UV absorbing compound, an optical brightener present in an amount sufficient to cause 10 visual illumination of the UV protective layer upon exposure to a light source and a polymeric base material of either a polyester, polycarbonate or acrylic. Upon exposure to a UV light or white light source the UV protective layer is visibly illuminated. A method of 15 detecting the UV protective layer in the UV stabilized multi-layer structure is also provided.

DESCRIPTION OF THE INVENTION

The production and installation difficulties 20 associated with UV stabilized multi-layer structures have now been overcome by addition of a very low level of an optical brightener to the UV protective layer. The very low level of the optical brightener renders the UV protective layer easily visible without interfering 25 with any essential functions of the UV absorbing compound.

The UV stabilized multi-layer structure of the present invention may be a sheet or film and comprises a UV protective layer and an underlying polymeric layer. 30 The polymeric layer is either a polyester or a polycarbonate. The UV protective layer, which is exposed to UV radiation and protects the polymeric layer, consists essentially of a UV absorbing compound, an optical brightener and a polymeric base material of 35 either a polyester, polycarbonate or acrylic. The UV

- 6 -

absorbing compound may be either fluorescing or non-fluorescing.

The optical brightener, which is a fluorescing material, is used at low levels to render the UV  
5 protective layer visible by either illumination with a white light or UV light source. The level of optical brightener can be as low as a few to tens of parts per million or as high as parts per thousands. The only real restriction on the upper level of usefulness of the  
10 optical brightener is that too high a level of optical brightener may give an overly bluish cast which could be found to be objectionable in some applications.  
Additionally, a higher level only results in added cost without a corresponding additional benefit in rendering  
15 the UV protective layer more readily visible.

In the multi-layer structure utilizing the fluorescing UV absorbing compound, the desirable level of optical brightener is between 1 and 1000 ppm based on the total amount of polymeric base material in the UV  
20 protective layer and is, preferably, between 1 and 100 ppm. The visual signal from the addition of these low levels of the optical brightener, i.e. between 1 and 100 ppm, is considerably stronger than that from even the fluorescing UV absorbing compound. The activating  
25 wavelength for fluorescence is also longer such that a strong, white light source can be used for visualization. Of course the UV protective layer is also readily visual utilizing a long wave UV light source.

30 For use with the non-fluorescing UV absorbing compound, the desirable level of optical brightener is between 10 and 1000 ppm based on the total amount of polymeric base material in the UV protective layer and is, preferably, between 50 and 200 ppm. The visual  
35 signal from the addition of low levels of the optical

- 7 -

brightener, i.e. between 10 and 200 ppm, is quite strong under long wave UV light illumination and enables easy visualization of the UV protective layer. At high enough levels of the optical brightener, i.e. above 200  
5 ppm, visualization of the UV protective layer occurs upon exposure to a strong, white light source.

The lower level of the optical brightener for use with the non-fluorescing UV absorbing compounds is restricted by the amount of non-fluorescing UV absorbing  
10 compound present and the fact that benzotriazoles, triazines, diphenylcyanoacrylates and the like tend to quench UV light without fluorescing. Thus, the lower level must be at least high enough to allow some of the exciting radiation to reach the optical brightening  
15 compound to activate its fluorescence. As compared to the fluorescing UV absorbing compounds, the lower level in the presence of the non-fluorescing compounds is significantly higher.

The lower limit is also dependent on the type of  
20 non-fluorescing UV absorbing compound and must, therefore, be determined for each individual case. For example, with a benzotriazole compound the lower limit is 25 ppm, whereas with a diphenylcyanoacrylate compound the lower limit is about 10 ppm. In most cases a level  
25 of 50 ppm works satisfactorily for any of the non-fluorescing UV absorbing compounds.

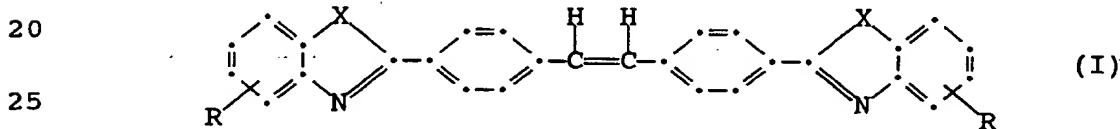
A benefit provided by the activation of the optical  
brightener using the white light source is that the  
30 layer containing the optical brightener can be easily seen in sunlight conditions and under fluorescent light illumination. Thus, someone installing such a structure could see the UV protective layer under sunlight conditions and would not even need the use of a strong auxiliary light source such as a flashlight.  
35 Furthermore, even though the UV protective layer

- 8 -

containing the optical brightener is very thin by comparison to the rest of the UV stabilized structure, the UV protective layer imparts an overall bluish cast to the entire sheet which is pleasing to the eye.

5 In addition, since the optical brightener is activated by longer wavelengths of light, the optical brightener is able to be seen not only under strong white light illumination but also when the light source is placed opposite to the UV protective layer. In that  
10 case even, the UV protective layer can still be clearly seen. Thus, confusion of production, installation or other personnel no longer exists.

A very wide range of optical brighteners may be employed in this invention. Many such compounds are  
15 disclosed in the prior art. One general class of such compounds are referred to in BE 641,426 and FR 1,397,727. These compounds are characterized by a general structure as shown below:



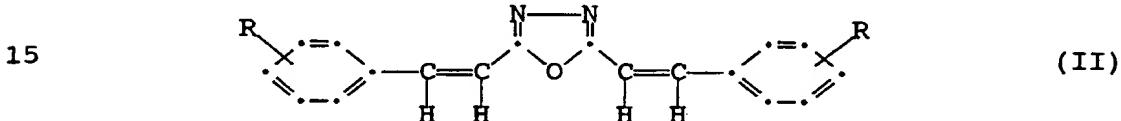
where R is an alkyl or aryl group of any desired length, generally less than 25 carbons, and X can be either S, O or NH. In general, the better optical brighteners are made with X equal to O and with R equal to H, a lower alkyl group of from 1 to 6 carbons or an aryl group such as benzene. Although the structures as shown are interpreted to be the cis-stilbene geometry, this is not a requirement. In the actual synthesis of the compound the double bond referred to can be cis-, trans- or a mixture of the two geometric isomers. More elaborate optical brighteners of this general system are enumerated in Helv. Chim Acta, 63, 413-19 (1980). For example, the benzoxazole ring may be changed via

- 9 -

substitution of a benzene ring carbon for a nitrogen. Thus, a great number of useful optical brighteners exist for use in this invention.

5 A preferred optical brightener for use in this invention belongs to the class of compounds referred to as benzoxazoles, i.e., where X is O in Structure I above. A more preferable compound is the parent compound itself where X = O and R = H.

10 Another class of optical brighteners useful in the present invention is represented by the following structure:



20 where R can be any desired group chosen from alkyl, aryl, halo, nitro, hydroxy, carboxy or alkyl or aryl ester of a carboxyl group. In general, the most useful group for this class of optical brighteners is where R is CO<sub>2</sub>R' wherein R' is a lower alkyl group of from 1 to 25 8 carbons. In addition, the preferred position of substitution is para for the R group. A more preferred optical brightener is where R is CO<sub>2</sub>Me and in the para position.

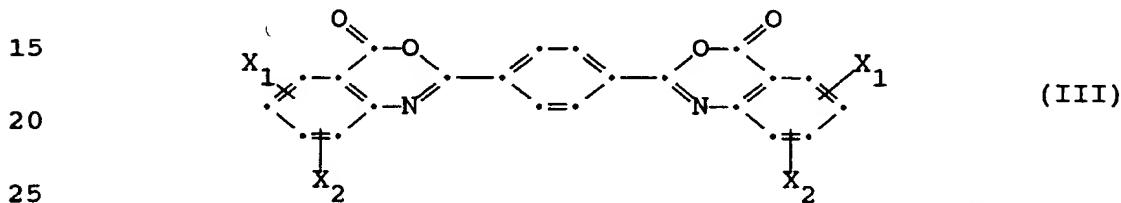
30 Many other classes of compounds useful as optical brighteners are also well known in the prior art, but are not specifically referred to herein. They are equally useful but are not readily commercially available.

35 A strong UV absorbing compound that is compatible with the polymer of the UV protective layer, i.e. polyesters, polycarbonates, or acrylics, is needed to insure that the polyester or polycarbonate in the underlying polymeric layer is protected against color shift when exposed in an outdoor environment. The UV

- 10 -

absorbing compound can be chosen from a large number of compounds well known in the art. The UV absorbing compound in the UV protective layer is typically present in concentrations of between 0.25 and 10 weight percent  
 5 based on the total weight of the UV absorbing compound and polymeric base material.

Fluorescing UV absorbing compounds useful to prevent yellowing of polyesters and polycarbonates come from the classes of compounds containing the  
 10 benzoxazinone ring system such as is disclosed in U.S. 4,446,262 or U.S. 5,264,539. The benzoxazinone absorbers are characterized by a structure



where  $X_1$  and  $X_2$  may be chosen from, but not limited to, the following functional groups: alkyl, aryl, heteroaryl, halo, alkoxy, aryloxy, hydroxy, carboxy, ester and nitro.  $X_1$  and  $X_2$  may also be hydrogen. Thus,  
 30 more than one functional group may be present on the benzoxazinone ring system itself. Where multiple functional groups are present they may be the same group or different groups.

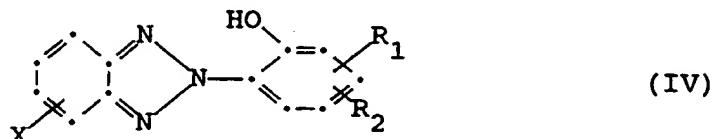
35 Additional benzoxazinone structures that are considered useful for stabilization of polyesters and polycarbonates against the harmful effects of outdoor weathering are give in U.S. 4,446,262 and U.S. 5,264,539.

40 Non-fluorescing UV absorbing compounds for use in the polyester, polycarbonate or acrylic based UV protective layer come from the classes of benzotriazoles, triazines or diphenylcyanoacrylates or

- 11 -

derivatives thereof. Representative compounds of the class of benzotriazole compounds are characterized by the structure:

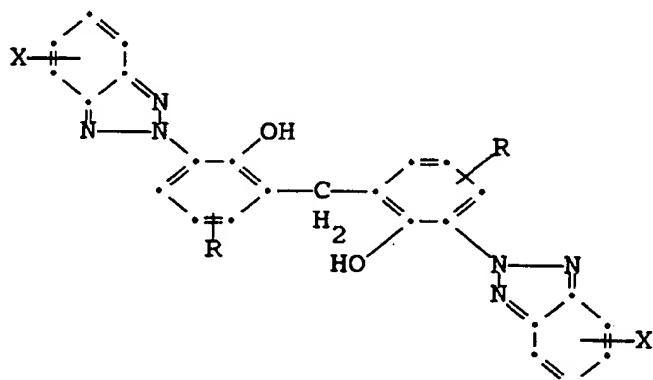
5  
10



where X is an alkyl or aryl substituent or a halogen atom such as chlorine and R<sub>1</sub> and R<sub>2</sub> are alkyl or aryl groups of from 1 to 20 carbon atoms or either one may be hydrogen. These groups may be located in any desired substitution pattern on the ring but are usually ortho-and/or para-to the hydroxyl group.

20 Benzotriazoles are also known to be prepared as essentially dimers of the compounds in Structure (IV) in order to reduce their volatility in the sheet manufacturing process. Such compounds are represented by the following structure:

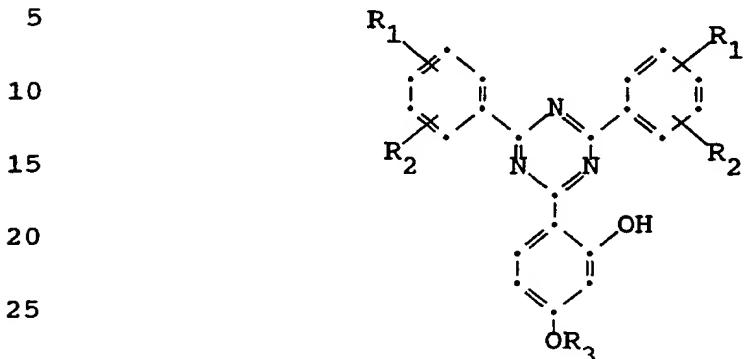
25  
30  
35  
40  
45  
50



where X and R have the same definition as for X and R<sub>1</sub>/R<sub>2</sub>, respectively, in Structure IV, except that R may not be hydrogen. The R group may be located at will on the ring but is usually located para-to the hydroxyl grouping for greatest synthetic ease.

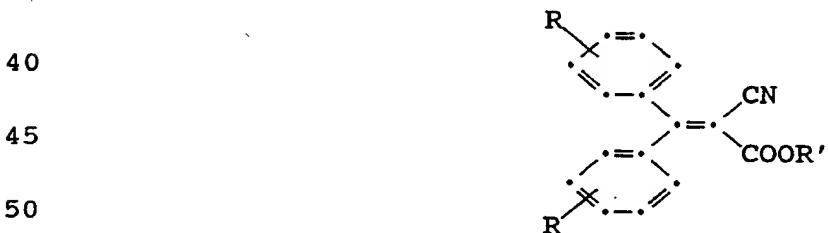
- 12 -

A representative structure from the class of triazine compounds useful as non-fluorescing UV absorbing compounds is as follows:



30 where  $R_1$ ,  $R_2$  and  $R_3$  are an alkyl or aryl group. Their position of substitution on the rings may be as desired but is generally ortho- and para- to the bond to the triazine ring for best synthetic ease. One or both of the two groups  $R_1$  or  $R_2$  may be hydrogen.

35 A representative structure for the diphenylcyanoacrylate class of compounds is as follows:



55 where R is an alkyl or aryl groups of from 1 to 20 carbons. Also R may contain a functional group such as carbomethoxy, hydroxy or an acid group or an ester group wherein the alcohol in the ester portion may be from 1 to 20 carbons. R' is an alkyl group of from 1 to 20 carbons. The alkyl groups referred to for both R and R' may be either linear or branched.

60            Polyesters suitable for use in both the UV  
protective layer and the polymeric layer may be any

- 13 -

polyester, modified polyester or copolyester. Particularly, suitable for the present invention is polyethylene terephthalate (PET) or any of its copolymers. Copolymers suitable for use may be prepared 5 from PET modified with 1,4-cyclohexanedimethanol wherein the 1,4-cyclohexanedimethanol (CHDM) component of the copolymer is present in from 1 to 99 mol percent. Other modifiers for PET include isophthalic acid and naphthalenedicarboxylic acid. Coglycols may also be 10 employed to prepare the copolymers. Limited examples of such coglycols include neopentyl glycol, 1,4-butanediol, diethylene glycol, 1,4-cyclohexane-dimethanol and 2,2,4,4-tetramethyl-1,3-cyclobutanediol. This list of modifying acids and glycols to produce 15 copolymers is a representative listing and, obviously, is not meant to be exhaustive.

Polycarbonates useful in either the UV protective layer or polymeric layer are generally chosen from bisphenol A polycarbonates or derivatives and/or 20 copolymers thereof. Examples of the derivatives include 3,3',5,5'-tetramethyl bisphenol A polycarbonate and 3,3',5,5'-tetrabromo bisphenol A polycarbonate. The bisphenol A may be substituted with any aryl or alkyl groups which do not interfere with the production of the 25 final polycarbonate and are generally tetra-substituted with the substituents being ortho to the phenolic -OH groups. Preferred polycarbonates are the parent bisphenol A polycarbonate and its copolymers with other bisphenols such as those described above.

30 Acrylics for use in the UV protective layer are chosen from homopolymers and/or copolymers of derivatives of methacrylic acid such as methyl methacrylate. Alkyl esters of methacrylic acid are the most commonly employed materials and are often 35 copolymerized with other alkyl esters of methacrylic

- 14 -

acid or acrylic acid such as ethyl acrylate, propyl acrylate, butyl acrylate, ethyl methacrylate, propyl methacrylate and butyl methacrylate. In addition, many such homo- or copolyacrylates are modified by the  
5 addition of a diene rubber or other rubbery compound that will result in higher impact properties of the acrylic material.

The UV protective layer which contains the UV absorbing compound and optical brightener need not be of  
10 the same composition as the polymeric layer which does not contain the UV absorbing compound and optical brightener. Thus, for example, a UV protective layer based on a copolymer of PET containing 31 mol % of  
15 moieties derived from CHDM could be mixed with the UV absorbing compound 2,2'-(1,4-phenylene)bis-4H-3,1-benzoxazin-4-one and the optical brightener 4,4'-bis(benzoxazoyl)stilbene (sold commercially under the trade name of Eastobrite OB-1 brightener from Eastman Chemical Company), which is then coextruded onto a much  
20 thicker layer of PET containing 12 mol % moieties derived from CHDM. The UV protective layer need not have more CHDM present in its polymeric base material than the CHDM content of the copolyester used for  
25 polymeric layer. The polymeric base material need not contain any CHDM or even be a polyester or copolyester, but may be chosen from any of the copolymers generally referred to above.

The polymers used in the UV protective layer and the polymeric layer may also be different polymers.  
30 Suitable combinations are set forth below:

- 15 -

Table I

	<u>UV Protective Layer</u> <u>Polymeric Base Material</u>	<u>Polymeric Layer</u>
5	Polyester/copolyester	Polycarbonate/ copolycarbonate
10	Polycarbonate/ copolycarbonate	Polyester/copolyester
10	Acrylic	Polyester/copolyester
15	Acrylic	Polycarbonate/ copolycarbonate
15	<p>The thickness of the UV protective layer on the underlying polymeric layer may vary according to the desired technological ends of said coating. The UV protective layer thickness will be governed by the concentration of UV absorbing compound. Together the thickness and concentration must create a UV protective layer that will absorb at least 90% of the harmful UV radiation prior to it reaching the underlying polymeric layer. More preferably the UV protective layer should absorb 99% of the harmful UV radiation and even more preferably 99.9% thereof. As a general rule, using the UV absorbing compound levels commonly used in the art, the UV protective layer need only be 1 to 2 mil in thickness in order to screen 99% of the incoming UV light contained in solar radiation. Obviously this minimum thickness may be further reduced by a higher concentration of the UV absorbing compound in the protective layer. This minimum UV protective layer thickness must be present in the final part. Thus, if a sheet is thermoformed to make the final desired part, the UV protective layer thickness must be the minimum even where the layer has been thinned out by the drawing down in the thermoforming process.</p>	
20		
25		
30		
35		

- 16 -

The UV stabilized multi-layer structure may be a film, a solid sheet, a profile or a hollow profile. In the hollow profile, as discussed in the background of the invention, the UV protective layer is placed on 5 either one side or both flat sides just the same as if it were a solid sheet.

The UV protective layer may be applied to the polymeric layer by coextrusion, lamination or coating technology. For example, the polymeric base material, 10 UV absorbing compound and the optical brightener may be extruded into a film of approximately 2 mils thickness. This film is subsequently laminated to a thicker sheet of polyester or polycarbonate. The final laminated structure will have all of the desirable properties of 15 good color retention and layer visualization as that in a coextruded structure. Solvent coating or casting technology are also suitable means of application of the UV protective layer to the polymeric layer.

20

#### EXAMPLES

In the examples UVCOR and xenon arc Weather-Ometer were artificial exposure devices used to simulate outdoor weathering. The following test procedure was employed for UVCOR. Sample plaques were cut to 3 by 4.5 25 in. (7.6 by 11.4 cm) and exposed in pairs. Exposure was conducted according to ASTM G53-93 in an Atlas Devices UVCOR equipped with 313 nm B bulbs (FS-40 lamps). The device was set to 70°C black panel temperature, condensing temperature of 40°C and an 8 hr light/4 hr 30 dark cycle. Samples were exposed in 96 hr increments, color measurement at each increment being followed by return to the device for further exposure.

For xenon arc Weather-Ometer, the following test procedure was employed. Sample plaques were cut to 2.5 35 by 5.5 in. (6.4 by 14.0 cm). The xenon arc

- 17 -

Weatherometer, Atlas Devices Ci65, was set to the following operating conditions: 0.35 W/m<sup>2</sup> flux at 340 nm, borosilicate inner and outer lamp filters, 63°C black panel temperature, 55% RH, 102 min. light only/18 min. light and water spray. The water spray was deionized water using a set of three F80 spray nozzles spraying on only the front side of the samples. The samples were exposed for 800, 1600, 2400, 3200, and 4000 kJ (measured at 340 nm).

Color measurement was accomplished using a HunterLab Ultrascan spectrophotometer in transmission mode following the current CIE recommendations to obtain L\*, a\* and b\* values. These conditions included a D65 light source, specular included mode and a 10 degree angle observer.

#### Example 1

This example illustrates the use of the optical brightener with a fluorescing absorbing compound in the UV protective layer in accordance with the invention. A coextrusion line was configured with a 3.5 in. (89 mm) main extruder and a 1.5 in. (38 mm) satellite extruder for application of a coextruded UV protective layer. The satellite extruder was connected by means of an adapter line to a Dow feedblock for 2 layer coextrusion. Both extruders, the adapter lines, the feedblock section and the sheeting die were set at 232°C (450°F). The sheeting die was placed in as close proximity as possible to the gap between rolls one and two of a vertical roll stack of three rolls (numbered from the top down). The extrudate was conducted downward in an s-wrap configuration. The main extruder was fed with polyethylene terephthalate copolyester containing 31 mol percent 1,4-cyclohexanedimethanol at a nominal IV of 0.75 dL/g (measured at 0.25 wt% in 60:40 weight:weight

- 18 -

phenol:tetrachloroethane). The satellite extruder was fed with a mixture of the same copolyester blended with a concentrate of 2,2'-(1,4-phenylene)bis-4H-3,1-benzoxazin-4-one made up in the same copolyester. The amount of concentrate was sufficient to give 3.2 wt% of the benzoxazinone in the final extruded UV protective layer. In addition, a concentrate of an optical brightener, 4,4'-bis(benzoxazoyl)stilbene (Eastobrite OB-1 available from Eastman Chemical Company of Kingsport, TN), in PET was added to give an overall concentration of 10 ppm of the optical brightener in the UV protective layer. The total sheeting thickness was held at 118 mils (3 mm) of which 4 to 5 mils (100 to 125 microns) was the UV protective layer.

Visualization of the UV protective layer by means of side illumination using a UV light was easily accomplished. Lighting of the side opposite from the UV protective layer likewise resulted in being able to see the UV protective layer as opposite to the direction of illumination by the UV light source. When the coextruded UV protective layer was reduced to 2 mils, it was still easily seen. Additionally, the UV protective layer could be seen in sunlight outdoors or in an office space lighted with fluorescent lights without any other illumination source irrespective of the direction of the illumination. The sheeting had an overall bluish cast when viewed from the edge.

#### Example 2

This example illustrates the differences between the prior art UV stabilized multi-layer structures and those of the present invention. The same extrusion setup and materials as in Example 1 were used to make 118 mil (3 mm) sheet except that the optical brightener concentrate was absent. The UV protective layer was

- 19 -

visible when illuminated from the same side, but effectively disappeared when illuminated from the back side of the sample, contrary to the behavior of the sheeting in Example 1. In addition, when the UV protective layer thickness was reduced to 2 mils (50 microns), an accurate measurement of the UV protective layer with a hand held microscope was difficult to obtain, also contrary to Example 1. Further, the UV protective layer could not be seen in sunlight conditions outdoors or in an office space lighted with fluorescent lights.

### **Example 3**

This example illustrates that addition of the optical brightener (OB) does not adversely affect the weathering properties of the UV stabilized multi-layer structure. Plaques cut from the sheeting of Examples 1 and 2, along with a control containing no UV absorbing compound and no optical brightener, were placed in UVCOR device and exposed as detailed above. The coloration of the plaques was measured by the b\* value since the L\* and a\* values did not change appreciably. Table 2 below shows the b\* values with exposure time.

Table 2

	<u>Exposure, Hours</u>	<u>b*</u> Values		
		<u>Example 1 sheeting (OB present)</u>	<u>Example 2 sheeting (no OB)</u>	<u>Unstabilized sheeting</u>
30	0	0.46	0.52	0.01
	96	1.80	1.98	5.46
	192	2.13	2.17	6.76
	288	2.34	2.18	7.33
	384	2.16	2.12	7.93

— 20 —

The retardation of color development was essentially the same for the plaque containing the optical brightener and UV absorbing compound (Example 1) vs the plaque that contained UV absorbing compound alone 5 (Example 2). Therefore, the presence of the optical brightener does not adversely affect weathering performance while simultaneously conferring the advantages of ease of layer visualization.

10      **Example 4**

This example illustrates that the optical brightener alone is not sufficient to control color development and must be used in conjunction with a strong UV absorbing compound. A film of polyethylene terephthalate copolyester containing 31 mol percent 15 1,4-cyclohexanediethanol at a nominal IV of 0.75 dL/g was extruded with enough concentrate of 4,4'-bis(benzoxazoyl)stilbene to give a final level of optical brightener in the copolyester film of 50 ppm along with 20 a control film. The film was exposed in a xenon arc Weather-Ometer and gave the following results as set forth in Table 3.

Table 3

b* Values					
	Exposure, Kilojoules	Sheeting Without OB Present		Sheeting With OB Present	
	0	4.50	(0)	4.00	(0)
30	800	5.13	(0.63)	4.22	(0.22)
	1600	6.32	(1.82)	5.11	(1.11)
	2400	7.27	(2.77)	6.52	(2.45)
	3200	8.02	(3.52)	7.40	(3.40)

35      The numbers in parenthesis are the change from the initial value and are shown for greater ease of

- 21 -

comparison. Although the films had a pleasing initial bluish edge color, it is readily apparent from the data that the rate of yellowing is essentially identical either with or without the optical brightener present.

- 5 Neither of these films contained a UV absorbing compound.

**Example 5**

This example illustrates the use of the optical  
10 brightener with the non-fluorescing UV absorbing compound in accordance with this invention. A 38 mm (1.5 inch) screw diameter extruder and film die were set at 232°C (450°F). The film die was placed in as close proximity as possible to the top roll of a vertical roll  
15 stack of two rolls. The extrudate was conducted downward in an s-wrap configuration. The extruder was fed with polyethylene terephthalate copolyester containing 31 mol percent 1,4-cyclohexanedimethanol at a nominal IV of 0.75 dL/g blended with a concentrate of  
20 bis[2-hydroxy-5-t-octyl-3-(benzotriazol-2-yl)phenyl]-methane prepared in the same copolyester. The amount of concentrate was sufficient to give 3 wt % of the benzotriazole compound in the final film. In addition,  
25 a concentrate of 4,4'-bis(benzoxazoyl)stilbene in the copolyester was added to give an overall concentration of optical brightener of 100 ppm in the UV protective layer. The film thickness was held at 5 mils (125 microns). This film was subsequently extrusion laminated to a 118 mil (3 mm) sheet of the same  
30 copolyester.

Visualization of the protected layer by means of side illumination using a UV light was easily accomplished. Lighting of the side opposite from the protected layer likewise resulted in being able to see

- 22 -

the layer as opposite to the direction of illumination by the UV light source.

**Example 6**

5        This example illustrates the difference between the prior art UV stabilized multi-layer structures and those of the present invention. The same sample preparation as in Example 5 was used to make 118 mil (3 mm) sheet with a 5 mil extrusion laminated film added  
10      except that the optical brightener concentrate was absent. The protected layer containing the UV absorbing compound was not visible when illuminated with a long wave UV light contrary to the behavior of the sheeting in Example 5.

15

**Example 7**

This example illustrates that addition of the optical brightener (OB) does not adversely affect the weathering properties of the resultant product. Plaques  
20      cut from the sheeting of Examples 5 and 6, along with a control containing no UV absorbing compound and no optical brightener, were placed in UVCONE device and exposed as detailed in Example 5. The coloration of the sample was measured by the b\* value. Table 4 shows b\*  
25      values with exposure time.

- 23 -

Table 4b\* Values

5	<u>Exposure, Hours</u>	<u>Example 5 Sheeting (OB Present)</u>	<u>Example 6 Sheeting (No OB)</u>	<u>Unstabilized Sheeting</u>	
	0	3.20 (0)	3.75 (0)	0.01	(0)
	96	4.64 (1.44)	5.11 (1.36)	5.46	(5.45)
10	192	5.94 (2.74)	5.51 (1.76)	6.76	(6.75)
	288	4.64 (1.44)	5.22 (1.47)	7.33	(7.32)
	384	4.83 (1.63)	5.35 (1.60)	7.93	(7.92)

The numbers in parenthesis are the change from the initial value and are shown for greater ease of comparison. The retardation of color development, which was significant over the control sample, was essentially the same for the sample containing the optical brightener and UV absorbing compound as compared to the sample that contained UV absorbing compound alone. Therefore, the presence of the optical brightener did not adversely affect weathering performance while simultaneously conferring the advantages of ease of layer visualization.

25

**Example 8**

This example illustrates that too low a level of optical brightener for the benzotriazole UV absorbing compound used in Example 5 does give the benefits of the invention. The extrusion of the film of Example 5 was repeated using a final level of the optical brightener of 10 ppm. The protected layer in the laminate was not readily visible.

35      **Example 9**

This example illustrates that too low a level of optical brightener for the benzotriazole UV absorbing

- 24 -

compound used in Example 5 when used instead with a diphenylcyanoacrylate absorbing compound gives the benefits of the invention. The extrusion of film of Example 5 was repeated using a final level of the 5 optical brightener of 10 ppm and 2-ethylhexyl-2-cyano-3,3-diphenylpropenoate as the UV absorbing compound at a concentration of 3 wt %. The protected layer in the laminate was readily visible under long wave UV illumination.

10

**Example 10**

This example illustrates that addition of the optical brightener does not adversely affect the weathering properties of the resultant product for a 15 diphenylcyanoacrylate UV absorbing compound system. Sheeting was prepared as in Example 5 using 2-ethylhexyl 2-cyano-3,3-diphenylpropenoate as the absorbing compound instead of the benzotriazole compound. The UV absorbing compound was present at 3 wt % as in Example 5. The 20 laminate was prepared in the same way as well. Plaques cut from this sheeting along with a control containing UV absorbing compound and no optical brightener (OB) were placed in a UVCOR device and exposed as detailed above. The coloration of the sample is measured by the 25 b\* value. Table 5 below shows the b\* values with exposure time.

- 25 -

Table 5

b\* Values

	<u>Exposure, Hours</u>	<u>OB Present</u>	<u>No OB</u>	
	0	0.78 (0)	0.45	(0)
	96	2.20 (1.42)	1.68	(1.23)
	192	2.47 (1.69)	2.24	(1.79)
5	288	2.66 (1.88)	2.35	(1.90)

The numbers in parenthesis are the change from the initial value and are shown for greater ease of comparison. The retardation of color development was 15 the same for the sample containing the optical brightener and UV absorbing compound as compared to the sample that contained UV absorbing compound alone. Therefore, the presence of the optical brightener did not adversely affect weathering performance while 20 simultaneously conferring the advantages of ease of layer visualization.

#### Example 11

This example illustrates the use of an optical 25 brightener in accordance with the invention. A 38 mm (1.5 inch) screw diameter extruder and film die were set at 280°C. The film die was placed in as close proximity as possible to the top roll of a vertical roll stack of two rolls. The extrudate was conducted downward in an 30 s-wrap configuration. The extruder was fed with polyethylene terephthalate copolyester at a nominal IV of 0.72 dL/g blended with a concentrate of 2,2'-(1,4-phenylene)bis-4H-3,1-benzoxazin-4-one prepared in the same copolyester. The amount of concentrate was 35 sufficient to give 3 wt % of the benzooxazinone compound in the final film. In addition, a concentrate of

- 26 -

4,4'-bis(benzoxazoyl)stilbene in the copolyester was added to give an overall concentration of 100 ppm of the optical brightener in the UV protective layer. The film thickness was held at 5 mils (125 microns). This film  
5 was subsequently extrusion laminated to a 60 mil (1.5 mm) sheet of the same copolyester.

Visualization of the UV protective layer by means of side illumination using a UV light was easily accomplished. Lighting of the side opposite from the UV  
10 protective layer likewise resulted in being able to see the layer as opposite to the direction of illumination by the UV light source. The UV protective layer was also visible under normal fluorescent lighting conditions, as well as in sunlight outdoors, as a bluish  
15 layer on the laminate. Omission of the optical brightener during the extrusion of the 5 mil film resulted in a laminate wherein the UV protective layer when visualized with a UV light source was not as easily seen and was not visible under fluorescent lighting or  
20 outdoor sunlight.

#### Example 12

This example illustrates the use of an optical brightener with polycarbonates in accordance with the  
25 invention. A 38 mm (1.5 inch) screw diameter extruder and film die were set at 280°C. The film die was placed in as close proximity as possible to the top roll of a vertical roll stack of two rolls. The extrudate was conducted downward in an s-wrap configuration. The  
30 extruder was fed with bisphenol A polycarbonate (Makrolon 2608 available from Bayer Corporation of Germany) blended with a concentrate of bis[2-hydroxy-5-t-octyl-3-(benzotriazol-2-yl)phenyl]methane prepared in the same polycarbonate. The amount of  
35 concentrate was sufficient to give 6 wt % of the

- 27 -

bis[2-hydroxy-5-t-octyl-3-(benzotriazol-2-yl)phenyl]-methane in the final film. In addition, a concentrate of 4,4'-bis(benzoxazoyl)-stilbene in polycarbonate was added to give an overall concentration of 100 ppm in the  
5 UV protective layer. The film thickness was held at 5 mils (125 microns). This film was subsequently extrusion laminated to a 118 mil (3 mm) sheet of the same polycarbonate.

Visualization of the UV protective layer by means  
10 of side illumination using a UV light was easily accomplished. Omission of the optical brightener during the extrusion resulted in a laminate that gave no indication of fluorescence in the UV protective layer. The UV protective layer was essentially indistinguishable from the rest of the laminate.  
15

**Example 13**

This example illustrates using an optical brightener with acrylics in accordance with the  
20 invention. A film was prepared from a copolymer of methyl methacrylate and ethyl acrylate containing 5 wt % of bis[2-hydroxy-5-t-octyl-3-(benzotriazol-2-yl)phenyl]-methane as the UV absorbing compound. In addition,  
25 4,4'-bis(benzoxazoyl)stilbene was added to give an overall concentration of 100 ppm in the acrylic UV protective layer. The UV protective layer was subsequently extrusion laminated to a 118 mil (3 mm) sheet of bisphenol A polycarbonate.

Visualization of the UV protective layer by means  
30 of side illumination using a UV light was easily accomplished owing to the bright blue-white color. Omission of the optical brightener during the extrusion resulted in a laminate that gave no indication of fluorescence in the UV protective layer. The UV

- 28 -

protective layer was essentially indistinguishable from the rest of the laminate.

The ease of visualization of the UV protective layer in the present invention due to the addition of 5 low levels of optical brightener results in being able to more readily measure the layer under production conditions and thereby be able to make production related adjustments to the thickness or thickness distribution of the layer. A convenient method for 10 installers to detect the UV protective layer of the UV stabilized structures is also provided by the present invention such that the direction of installation, i.e. having the UV protective layer face the direction of the radiation exposure of a panel, is easily determined.

15 The invention has been described in detail with particular reference to preferred embodiments thereof, but it will be understood that variations and modifications can be effected within the spirit and scope of the invention.

20

- 29 -

CLAIMS

We claim:

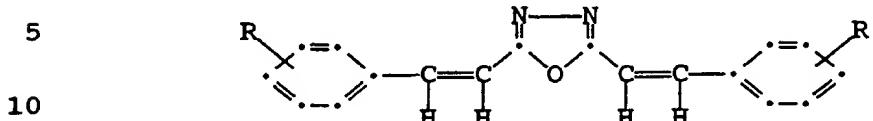
1. A UV stabilized multi-layer structure comprising:
  - 5 a) a UV protective layer comprising a UV absorbing compound; a polymeric base material selected from the group consisting of a polyester, an acrylic and a polycarbonate; and an optical brightener present in an amount sufficient to cause visual illumination of the UV protective layer upon exposure to a light source; and
    - 10 b) a polymeric layer comprising a polyester or a polycarbonate.
2. The structure as recited in Claim 1 wherein the UV 15 absorbing compound is a fluorescing material, the optical brightener is present in an amount between 1 and 1000 ppm based on the total amount of the polymeric base material in the UV protective layer and the light source is an UV light or a white light.
- 20 3. The structure as recited in Claim 2 wherein the fluorescing material is a benzoxazinones.
4. The structure as recited in Claim 2 wherein the 25 optical brightener is present in an amount between 1 and 100 ppm.
5. The structure as recited in Claim 1 wherein the UV absorbing compound is a non-fluorescing material, the 30 optical brightener is present in an amount between 10 and 1000 ppm based on the total amount of the polymeric base material in the UV protective layer and the light source is an UV light.

- 30 -

6. The structure as recited in Claim 5 wherein the optical brightener is present in an amount between 50 and 200 ppm.
- 5 7. The structure as recited in Claim 5 wherein the non-fluorescing material is selected from the group consisting of benzotriazoles, triazines and diphenylcyanoacrylates.
- 10 8. The structure as recited in Claim 1 wherein the UV absorbing compound is a non-fluorescing material, the optical brightener is present in an amount between 200 and 1000 ppm based on the total amount of the polymeric base material in the UV protective layer and the light source is a white light.
- 15
9. The structure as recited in Claim 8 wherein the non-fluorescing material is selected from the group consisting of benzotriazoles, triazines and diphenylcyanoacrylates.
- 20
10. The structure as recited in claim 1 wherein the optical brightener has the general chemical structure:
- 25
- 30
- 
- where R is an alkyl or aryl group and X is S, O or NH.
- 35 11. The structure as recited in claim 10 wherein for the optical brightener X is O and R is H, a lower alkyl group of from 1 to 6 carbons or an aryl group.

- 31 -

12. The structure as recited in claim 1 wherein the UV absorbing compound is non-fluorescing and the optical brightener has the general chemical structure:



where R is alkyl, aryl, halo, nitro, hydroxy, carboxy, or alkyl or aryl ester of a carboxyl group.

15 13. The structure as recited in claim 12 wherein for  
the optical brightener R is  $\text{CO}_2\text{R}'$  wherein  $\text{R}'$  is an alkyl  
group of from 1 to 8 carbons.

14. The structure as recited in claim 12 wherein for  
20 the optical brightener R is in the para position of  
substitution for the R group.

15. A method of detecting a UV protective layer in a UV  
stabilized multi-layer structure comprising the steps  
25 of:

(a) preparing a UV stabilized multi-layer structure having

(1) a UV protective layer comprising a UV absorbing compound; a polymeric base material selected from the group consisting of a polyester, an acrylic and a polycarbonate; and an optical brightener present in an amount sufficient to cause visual illumination of the UV protective layer upon exposure to a light source; and

(2) a polymeric layer comprising a polyester or a polycarbonate;

(b) applying a light source to the UV stabilized multi-layer structure; and

- 32 -

(c) visibly determining the location of the UV protective layer by its illumination.

16. The method as recited in claim 15 wherein the UV  
5 absorbing compound is a fluorescing material, the optical brightener is present in an amount between 1 and 1000 ppm based on the total amount of polymeric base material and the light source is a white light or an UV light.

10

17. The method as recited in claim 15 wherein the UV absorbing compound is a non-fluorescing material, the optical brightener is present in an amount between 10 and 1000 ppm based on the total amount of polymeric base  
15 material and the light source is an UV light.

18. The method as recited in claim 15 wherein the UV absorbing compound is a non-fluorescing material, the optical brightener is present in an amount between 200 and 1000 ppm based on the total amount of polymeric base  
20 material and the light source is a white light.

# INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 97/19895

**A. CLASSIFICATION OF SUBJECT MATTER**

IPC 6	B32B27/18	B32B27/36	C08K5/00	C08K5/315	C08K5/35
	C08L67/00	C08L33/00	C08L69/00		

According to International Patent Classification(IPC) or to both national classification and IPC

**B. FIELDS SEARCHED**

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 B32B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	DE 41 25 857 A (ROEHM GMBH) 4 February 1993 see page 2, line 65 - page 3, line 57 see page 5, line 31 - line 56 ---	1,2,4-7
X	WO 92 17535 A (RED SPOT PAINT & VARNISH) 15 October 1992 see claims 1,3,6 see page 8, line 34 - page 9, line 16; example 2 ---	1,5,6
A	EP 0 679 614 A (CENTRAL GLASS CO LTD) 2 November 1995 see claims see page 4, line 43 - page 5, line 10 ---	1 -/-

Further documents are listed in the continuation of box C.

Patent family members are listed in annex.

\* Special categories of cited documents :

- "A" document defining the general state of the art which is not considered to be of particular relevance"
- "E" earlier document but published on or after the international filing date
- "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- "O" document referring to an oral disclosure, use, exhibition or other means
- "P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

1

Date of the actual completion of the international search

7 April 1998

Date of mailing of the international search report

24/04/1998

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2  
NL - 2280 HV Rijswijk  
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl.  
Fax: (+31-70) 340-3016

Authorized officer

Ibarrola Torres, O

## INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 97/19895

## C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	DATABASE WPI Section Ch, Week 9538 Derwent Publications Ltd., London, GB; Class A26, AN 95-290072 XP002061648 & JP 07 187 717 A (CENTRAL GLASS CO LTD) , 25 July 1995 see abstract ----- US 4 895 787 A (PLATZER STEPHAN J W) 23 January 1990 see column 3, line 39 - column 4, line 34 see column 5, line 57 - column 6, line 68 -----	1
A		1

**INTERNATIONAL SEARCH REPORT**

Information on patent family members

International Application No

PCT/US 97/19895

Patent document cited in search report	Publication date	Patent family member(s)		Publication date
DE 4125857 A	04-02-93	AT 134672 T CA 2075216 A DE 59205452 D EP 0528196 A ES 2084888 T JP 5222263 A		15-03-96 04-02-93 04-04-96 24-02-93 16-05-96 31-08-93
WO 9217535 A	15-10-92	AU 665948 B AU 1902292 A BR 9205855 A CA 2107353 A CZ 9302048 A EP 0581872 A JP 5098187 A MX 9201529 A		25-01-96 02-11-92 27-09-94 04-10-92 16-03-94 09-02-94 20-04-93 01-10-92
EP 0679614 A	02-11-95	JP 7291667 A DE 69500433 D DE 69500433 T US 5683804 A		07-11-95 21-08-97 06-11-97 04-11-97
US 4895787 A	23-01-90	AU 3818489 A CA 1336947 A DE 68925313 D DE 68925313 T EP 0352055 A JP 2066547 A US 5049476 A US 5236806 A		18-01-90 12-09-95 15-02-96 20-06-96 24-01-90 06-03-90 17-09-91 17-08-93